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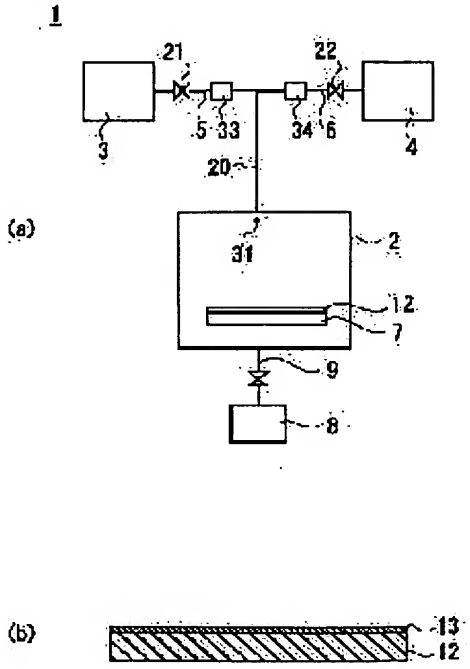
(54) METHOD FOR DEPOSITING TRANSMISSION ELEMENT SILICIDE THIN FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a technique for depositing a transition element silicide thin film of high film quality, being free from contamination with silicon carbide.
SOLUTION: In this film deposition method, gaseous organometallic compound containing a carbonyl group and a gaseous silicon starting material are mixed in an introduction tube 20, this mixture is thereafter charged into a vacuum tank 2, and a metallic silicide thin film is vapor-phase-grown on the surface of a preheated silicon substrate 12. At the time of using the gaseous organometallic compound containing a carbonyl group as a source gas in this way, carbon atoms in the gas are made into gaseous carbon monoxide, are absorbed into a vapor phase and are discharged to the outside of the vacuum tank without being deposited on the surface of the silicon substrate 12. Thus the metallic silicide thin film of high quality without contamination with silicon carbide can be obtained.



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CLAIMS

[Claim(s)]
[Claim 1] The membrane formation approach of the transition element silicide thin film which is the membrane formation approach of the transition element silicide thin film to which introduce the transition element material gas containing the metal atom belonging to a transition element, and the silicon material gas containing a silicon atom in a reaction chamber, and the front face of said silicon substrate is made to carry out vapor growth of the transition element silicide thin film, and is characterized by using the gas of the organometallic compound which at least one or more carbonyl groups come to combine with said metal atom as said transition element material gas.
[Claim 2] The membrane formation approach of the transition element silicide thin film according to claim 1 characterized by using the gas containing any one or more sorts of silane gas, disilane gas, or organic silicon gas as said silicon material gas.
[Claim 3] The membrane formation approach of the transition element silicide thin film according to claim 1 or 2 characterized by using both Fe(CO) 5 gas, or Fe(CO) 12 both [either or] as gas of said organometallic compound.
[Claim 4] The membrane formation approach of the transition element silicide thin film of claim 1 characterized by introducing in said reaction chamber after mixing said transition element material gas and said silicon material gas thru/or claim 3 given in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to an improvement of the manufacture approach of the iron silicide thin film used for luminescence, a photo detector, etc. about the manufacture approach of a transition element silicide thin film.
[0002]
[Description of the Prior Art] In recent years, luminescence and the photo detector which serves both as a light emitting device and a photo detector with one component are proposed. An example of this luminescence and photo detector is shown in the sign 115 of drawing 5 (a) and (b). Drawing 5 (a) is the top view of luminescence and a photo detector 115, and this drawing (b) is an A-A line sectional view of this drawing (a). This luminescence and photo detector 115 have the silicon substrate 112 of n mold. The iron silicide thin film 113 is formed all over the front face of a silicon substrate 112. As shown in drawing 5 (b), the surface electrode 114 which consists of a ring-like metal thin film is formed in the front face of the iron silicide thin film 113, and all over another side and the rear face of a silicon substrate 112, the rear-face electrode 111 which consists of a metal is formed.
[0003] In this luminescence and photo detector 115, since a silicon substrate 112 is n mold and another side and the iron silicide thin film 113 are p molds, pn junction is formed between the iron silicide thin film 113 and the silicon substrate 112. The surface electrode 114 is formed in the shape of a ring, and has exposed the iron silicide thin film 113.
[0004] By this luminescence and photo detector 115, where the load which is not illustrated between a surface electrode 114 and the rear-face electrode 111 is connected, if sunlight carries out incidence to the iron silicide thin film 113, a current will flow in the direction of the iron silicide thin film 113 of p mold from the silicon substrate 112 of n mold, and the current will be supplied to a load by the photovoltaic effect. In this case, luminescence and a photo detector 115 function as a photo detector which light is received [photo detector] and generates electromotive force.
[0005] On the other hand, if a negative electrical potential difference is impressed to the rear-face electrode 111 while impressing a forward electrical potential difference to a surface electrode 114, an electron hole is injected into the silicon substrate 112 of n mold from the iron silicide thin film 113 of p mold, and it recombines with an electron, and the binding energy will be changed into light and will emit light. Practically, a p-type silicon layer is formed on the iron silicide thin film 113, and an electron hole may be made to be poured in also from the p-type silicon layer. In this case, luminescence and a photo detector 115 function as a light emitting device. Thus, luminescence and a photo detector 115 are components which served as the function of both a light emitting device and a photo detector.
[0006] In order to manufacture luminescence and the photo detector 115 of a configuration of having mentioned above, it is necessary to form an iron silicide thin film to a silicon substrate surface. Iron is vapor-deposited to a silicon substrate surface, and there are vacuum deposition which silicide-izes this by carrying out heating maintenance at about 400 degrees C, the pouring-in method which drives iron ion into a silicon substrate surface, and forms silicide by subsequent heat treatment in the approach of forming iron silicide in a silicon substrate surface. However, by these vacuum deposition or pouring-in methods, iron silicide is condensed in the shape of an island in a silicon substrate surface, or is formed granular, and is not formed in the shape of a thin film. For this reason, the CVD method is used for forming a thin film.

[0007] An example of the CVD membrane formation equipment used for the sign 101 of drawing 6 forming an iron silicide thin film is shown. This CVD membrane formation equipment 101 has the vacuum tub 102. The evacuation system 108 is connected to the vacuum tub 102, and it is constituted so that evacuation of the interior can be carried out.
[0008] The installation base 107 is arranged at the interior lower part of vacuum tub 102. The interior is equipped with a heater, and that front face is made flat, and this installation base 107 is constituted so that the temperature up of the substrate can be carried out, where a substrate is laid in that front face.
[0009] The end of the gas installation tubing 105 and 106 is connected to the vacuum tub 102. The other end of the gas installation tubing 105 and 106 is connected to the gas installation equipments 103 and 104, respectively. Bulbs 121 and 122 are formed, respectively and the gas installation equipments 103 and 104 are filled up with mono-silane (SiH4) gas and metallocene (Fe2 (C5H5)) gas, respectively, and it is constituted by each gas installation tubing 105 and 106 so that mono-silane gas and metallocene gas can be introduced in the vacuum tub 102 from the gas installation tubing 105 and 106, respectively. In each gas installation tubing 105 and 106, flow regulators 133 and 134 are formed, respectively, and it is constituted so that the flow rate of the mono-silane gas introduced in the vacuum tub 102 and metallocene gas can be adjusted, respectively.
[0010] In order to form an iron silicide thin film to a silicon substrate surface using this CVD membrane formation equipment 101, evacuation of the inside of the vacuum tub 102 is carried out first, where an internal vacua is maintained, a silicon substrate is carried in in the vacuum tub 102, and it lays in installation base 107 front face. The silicon substrate of the condition is shown in the sign 112 of drawing 6 R> 6.
[0011] The installation base 107 is beforehand heated at the heater, and if a silicon substrate 112 is laid in installation base 107 front face, the temperature up of the silicon substrate 112 will be carried out. If the temperature up of the silicon substrate 112 is carried out to predetermined temperature, while flow regulators 133 and 134 will adjust mono-silane gas and metallocene gas to a suitable flow rate, it introduces in the vacuum tub 102 from the gas installation tubing 105 and 106, respectively.
[0012] Then, iron silicide carries out vapor growth on silicon substrate 112 front face, and an iron silicide thin film is formed by silicon substrate 112 front face. If this CVD method is used, the thin film of a large area can be formed to a silicon substrate surface.
[0013] However, in an above-mentioned CVD method, metallocene gas is used as material gas, the carbon contained in metallocene gas during thin film growth will mix into iron silicide, and carbonization silicon will be formed into an iron silicide thin film. For this reason, the membraneous quality of a thin film deteriorated and the problem that only the membraneous quality which is equal to use of luminescence and a photo detector was no longer obtained had arisen.
[0014]
[Problem(s) to be Solved by the Invention] Created in order that this invention may solve un-arranging [of the above-mentioned conventional technique], the purpose has membraneous quality in offering the membrane formation approach which can form a good transition element silicide thin film.
[0015]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, invention according to claim 1 The transition element material gas containing the metal atom belonging to a transition element and the silicon material gas containing a silicon atom are introduced in a reaction chamber. It is the membrane formation approach of the transition element silicide thin film to which the front face of said silicon substrate is made to carry out vapor growth of the transition element silicide thin film, and is characterized by using the gas of the organometallic compound which at least one or more carbonyl groups come to combine with said metal atom as said transition element material gas. Invention according to claim 2 is the membrane formation approach of a transition element silicide thin film according to claim 1, and is characterized by using the gas containing any one or more sorts of silane gas, disilane gas, or organic silicon gas as said silicon material gas. Invention according to claim 3 is the membrane formation approach of a transition element silicide thin film according to claim 1 or 2, and is characterized by using both Fe(CO) 5 gas, or Fe(CO) 12 both [either or] as gas of said organometallic compound. Invention according to claim 4 is the membrane formation approach of the transition element silicide thin film of claim 1 thru/or claim 3 given in any 1 term, and after it mixes said transition element material gas and said silicon material gas, it is characterized by introducing in said reaction chamber.

[0016] For example, the silicon substrate surface is made to carry out vapor growth of the transition element silicide by making a substrate heat like Fe(CO) 5 gas by this invention, using the gas of the organometallic compound which one or more carbonyl groups are combined with a metal atom, and changes, and silicon material gas, such as for example, silane gas, as material gas.
[0017] Although the carbon atom is contained in the carbonyl group, since this carbon atom becomes carbon monoxide gas at the time of vapor growth, is absorbed by the gaseous phase and discharged out of a reaction chamber, it does not adhere to a substrate front face. Therefore, unlike the conventional approach using the metallocene gas which is organic metal gas by which one piece does not contain a carbonyl group, either, silicon carbide does not mix into a silicide thin film. Therefore, the good thin film of the membraneous quality which does not contain silicon carbide can be formed.
[0018] In the membrane formation approach of this invention, in addition, the gas of the organometallic compound which has one or more carbonyl groups like Fe(CO) 5 gas Although a metal may deposit on the internal wall surface of the reaction chamber near an inlet since near the inlet to a reaction chamber is an elevated temperature when it introduces into a reaction chamber through the inlet established in the reaction chamber By the membrane formation approach of this invention, after mixing silicon material gas and the gas of an organometallic compound beforehand, it has introduced into a reaction chamber. In this case, it reacts mutually by silicon material gas and the gas of an organometallic compound being mixed, and an iron silicide thin film can be formed, without iron depositing and adhering to the internal wall surface of the reaction chamber near an inlet, since the intermediate product which maintains the condition of gas also at an elevated temperature is generated.
[0019]
[Embodiment of the Invention] With reference to a drawing, the operation gestalt of this invention is explained below. It is equipment which enforces the membrane formation approach of this operation gestalt to the sign 1 of drawing 1 (a), and an example of the CVD membrane formation equipment used for membrane formation of an iron silicide thin film is shown.
[0020] This CVD membrane formation equipment 1 has the vacuum tub 2 which is an example of a reaction chamber used for the membrane formation approach of this invention. The evacuation system 8 is connected to the vacuum tub 2, and it is constituted so that evacuation of the interior can be carried out.
[0021] The installation base 7 is arranged at the interior lower part of vacuum tub 2. It has the heater which is not illustrated to that interior, and that front face is made flat, and this installation base 7 is constituted so that the temperature up of the substrate may be carried out, where a substrate is laid in that front face.
[0022] Two gas installation equipments 3 and 4 are formed in the vacuum tub 2 exterior. Each gas installation equipments 3 and 4 are filled up with the silicon material gas which contains a silicon atom, respectively, and the transition element material gas containing the metal atom belonging to a transition element. With this operation gestalt, iron PENTA carbonyl (Fe5 (CO)) gas is used as transition element material gas, using mono-silane (SiH4) gas as silicon material gas. Among these, the near gas installation equipment 4 with which it fills up with iron PENTA carbonyl gas has the cooling system in the interior, and is changing it into the condition of having cooled the iron PENTA carbonyl gas with which the interior was filled up at -5 degrees C.
[0023] The end of the gas-evolution tubing 5 and 6 is connected to each gas installation equipments 3 and 4, respectively. It connects with the end of the introductory tubing 20, and bulbs 21 and 22 are formed in each gas-evolution tubing 5 and 6, respectively, and if each bulbs 21 and 22 are opened, both the other ends of each gas-evolution tubing 5 and 6 are constituted so that mono-silane gas and iron PENTA carbonyl gas can be introduced to the introductory tubing 20 interior through the gas-evolution tubing 5 and 6, respectively. It connects with the inlet 31 established in the vacuum tub 2, and if mono-silane gas and iron PENTA carbonyl gas are introduced into the introductory tubing 20, the other end of the introductory tubing 20 is constituted so that it may be introduced from an inlet 31 in the vacuum tub 2 interior, after being mixed in the introductory tubing 20 interior. Flow regulators 33 and 34 are formed, respectively, and after adjusting the flow rate of mono-silane gas and iron PENTA carbonyl gas to a suitable flow rate, it is constituted by each gas-evolution tubing 5 and 6 so that it can introduce in the vacuum tub 2 through the introductory tubing 20.
[0024] In order to form an iron silicide thin film to a silicon substrate surface using the CVD membrane formation equipment 1 of a configuration of having mentioned above, evacuation of the inside of the vacuum tub 2 is carried out first, where an internal vacua is maintained, a silicon substrate is carried in in the vacuum

tub 2, and it lays in installation base 7 front face. The silicon substrate of the condition is shown in the sign 12 of drawing 1 .

[0025] The installation base 7 is beforehand heated at the heater, and if laid in installation base 7 front face, the temperature up of the silicon substrate 12 will be carried out. It introduces to the introductory tubing 20, respectively, opening each bulbs 21 and 22, starting flow regulators 33 and 34, and adjusting mono-silane gas and iron PENTA carbonyl gas to a suitable flow rate, if the temperature up of the silicon substrate 12 is carried out to predetermined membrane formation temperature (500 degrees C). Then, mono-silane gas and iron PENTA carbonyl gas are mixed within the introductory tubing 20, and the mixed gas is introduced into the vacuum tub 2. The flow rate of mono-silane gas and iron PENTA carbonyl gas is adjusted, respectively, the flow rate of mono-silane gas and iron PENTA carbonyl gas is set to 2:1, and it is made for the pressure of the vacuum tub 2 interior to be set to 3x10 to 2 Pa with each flow regulators 33 and 34 at this time.

[0026] Then, iron silicide carries out vapor growth to the front face of a silicon substrate 12, and an iron silicide thin film is formed by the front face of a silicon substrate 12. The iron silicide thin film is shown in the sign 13 of drawing 1 (b).

[0027] Then, the inside of the vacuum tub 2 is exhausted and substrate temperature is cooled at 100 degrees C or less in the hydrogen ambient atmosphere of about 1x10 - 1Pa. Then, the inside of the vacuum tub 2 is returned to atmospheric pressure, and a silicon substrate 12 is taken out to the vacuum tub 2 exterior.

[0028] By the membrane formation approach of this operation gestalt, although the carbon atom is mixing as transition element material gas also into the **** cage for iron PENTA carbonyl gas, and its iron PENTA carbonyl gas, this iron PENTA carbonyl gas has five carbonyl groups. For this reason, during thin film growth, since it is exhausted out of a vacuum tub, without being absorbed in a gaseous phase as carbon monoxide gas, and adhering to a substrate front face and silicon carbide does not mix into a thin film, a carbon atom can form the good thin film of membraneous quality.

[0029] That the effectiveness of the membrane formation approach mentioned above should be checked, the artificer of this invention etc. made growth time amount 1 hour, formed the iron silicide thin film to the silicon substrate surface, and investigated the property of the iron silicide thin film.

[0030] Drawing 2 is a graph which shows the evaluation result of the X diffraction in an iron silicide thin film. The axis of abscissa of drawing 2 shows location 2theta of diffraction, and the axis of ordinate shows the dispersion reinforcement of the direction of 2theta. The curve (A) of drawing 2 shows the evaluation result of the iron silicide thin film formed with the CVD method of this operation gestalt, and the curve (B) of drawing 2 shows the evaluation result about the iron silicide thin film formed with the conventional CVD method which used metallocene gas for source gas. Moreover, both the signs 40, 46, 47, 48, 50, 56, 57, and 58 show the spectrum of the silicon atom in an iron silicide thin film in drawing 2 , and both the signs 45 and 55 show the spectrum of iron silicide. Moreover, signs 41, 42, 43, and 44 show the spectrum of carbonization silicon.

[0031] Although the spectrums 40, 46, 47, 48, 50, 56, 57, and 58 of a silicon atom have appeared also in any of a curve (A) and (B), in a curve (A), the spectrum of carbonization silicon has not appeared at all to the spectrums 41, 42, 43, and 44 of carbonization silicon having appeared at a curve (B). Furthermore, as compared with the spectrum 45 of iron silicide [in / in the spectrum 55 of the iron silicide in a curve (A) / a curve (B)], the peak value is large. As mentioned above, in the CVD method of this operation gestalt, it turns out that carbonization silicon cannot mix but the good iron silicide thin film of membraneous quality can be formed as compared with the former.

[0032] Moreover, the artificer of this invention etc. analyzed the iron silicide thin film formed by the silicon substrate surface by the membrane formation approach of this operation gestalt with Auger electron spectroscopy. Drawing 3 is a graph which shows the evaluation result of the Auger-electron-spectroscopy analysis method of the iron silicide thin film formed by the membrane formation approach of this operation gestalt.

[0033] The axis of abscissa of drawing 3 shows spatter time amount. This spatter time amount supports the depth of the direction of thickness of an iron silicide thin film. Moreover, the axis of ordinate shows the spectral intensity of an Auger electron, and supports the element concentration in a thin film.

[0034] The curve in drawing 3 (C) shows the spectrum of a silicon atom, and the curve (D) shows the spectrum of an iron atom. Moreover, a curve (E) shows the spectrum of an oxygen atom and the curve (F) shows the spectrum of a carbon atom.

[0035] as shown in drawing 3 , to the curve (C) and the curve (D) having appeared by the reinforcement of about 1 law, near the front face, it is only appearing slightly and a curve (E) and a curve (F) have hardly appeared in the iron silicide thin film of this operation gestalt. as mentioned above, in this iron silicide thin film, although the iron atom and the silicon atom exist at a rate of about 1 law, even if the carbon atom and the oxygen atom exist, it will turn out that it is the amount of below limit-of-detection extent. Also from this, it has checked that a carbon atom hardly mixed into an iron silicide thin film with the CVD method of this operation gestalt.
[0036] Furthermore, the artificer of this invention etc. investigated the intensity distribution of surface luminescence produced on a thin film front face, when a laser beam was irradiated on the iron silicide thin film front face formed by the silicon substrate surface by the membrane formation approach of this operation gestalt.

[0037] Drawing 4 is drawing showing luminescence intensity distribution when a laser beam is irradiated and carries out surface luminescence on an iron silicide thin film front face. The axis of abscissa of drawing 4 shows the measurement wavelength of the light which emitted light, and the axis of ordinate shows luminescence reinforcement. The curve in drawing 4 (H) shows the spectrum of the luminescence reinforcement of the iron silicide thin film formed by the membrane formation approach of this operation gestalt, and the curve (I) shows the spectrum of the luminescence reinforcement of the iron silicide thin film formed by the conventional membrane formation approach, using ferrocene (C5H5) Fe (C5H5) gas as source gas.
[0038] Although the spectrum is fixed, the spectrum of luminescence reinforcement does not appear at all and surface luminescence has not arisen at all with the curve (I) corresponding to the iron silicide thin film formed using ferrocene gas, it turns out with a curve (H) that the peak 50 of the spectrum near 15600nm with big measurement wavelength appeared, and strong surface luminescence has appeared. In addition, if only iron PENTA carbonyl gas is independently introduced in the vacuum tub 2 in case iron PENTA carbonyl gas is introduced into the vacuum tub 2 interior, as mentioned above Although iron may deposit and adhere to the internal wall surface of the vacuum tub 2 near an inlet since the temperature near [where iron PENTA carbonyl gas is introduced in a vacuum tub] an inlet becomes an elevated temperature 200 degrees C or more By the membrane formation approach of this operation gestalt, it has introduced into the vacuum tub 2 interior, after mixing iron PENTA carbonyl gas and mono-silane gas within the introductory tubing 20. For this reason, iron PENTA carbonyl gas and mono-silane gas react in the introductory tubing 20 interior, and the gas of an intermediate product is formed. This intermediate product is more expensive than ordinary temperature, and it can form an iron silicide thin film, without iron depositing and adhering to a gas inlet 31, since a gaseous condition is maintained in temperature (about 200 degrees C) extent inside [vacuum tub 2] the gas inlet 31 neighborhood which is temperature lower than the substrate temperature at the time of membrane formation.
[0039] Moreover, with this operation gestalt, although iron PENTA carbonyl gas (Fe5 (CO)) is used as transition element material gas, the transition element material gas used in case an iron silicide thin film is formed is not restricted to this, and may use iron dodecane carbonyl (Fe12 (CO)) gas.
[0040] Moreover, with this operation gestalt, although the iron silicide thin film is formed, the transition element silicide thin film of this invention is applicable not only to this but membrane formation of for example, tungsten silicide and titanium silicide. What is necessary is just to use titanium hexa carbonyl (Ti6 (CO)) gas as transition element material gas that what is necessary is just to use tungsten hexa carbonyl (W (CO) 6) gas as transition element material gas in forming a tungsten silicide thin film at this time, in forming a titanium silicide thin film.
[0041] Moreover, although mono-silane (SiH4) gas was used as silicon material gas, the silicon material gas of this invention is not restricted to this, and may use other silane system gas like disilane (Si2H6) gas, for example, may use organic silicon gas.
[0042] Furthermore, although the mono-silane gas which was made to link the gas-evolution tubing 5 and 6 and the introductory tubing 20 directly, and was emitted from each gas-evolution tubing 5 and 6, and iron PENTA carbonyl gas are mixed in the introductory tubing 20 interior in this operation gestalt After preparing a mixing chamber not only between this but between the gas-evolution tubing 5 and 6 and the introductory tubing 20 and mixing mono-silane gas and iron PENTA carbonyl gas in this mixing chamber, this invention may be constituted so that that mixed gas may be introduced from the introductory tubing 20 to the vacuum tub 2 interior.

[0043]
[Effect of the Invention] The good transition element silicide thin film of membraneous quality can be formed.

[Translation done.]

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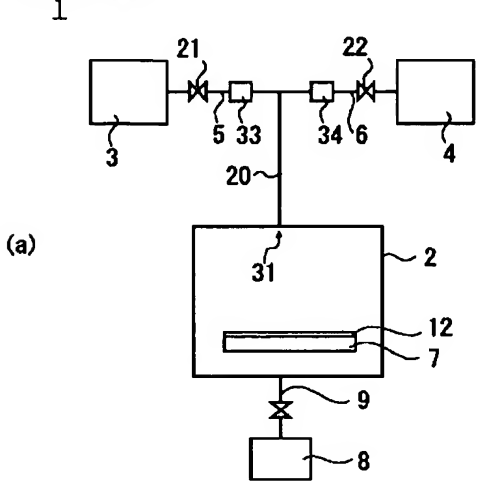
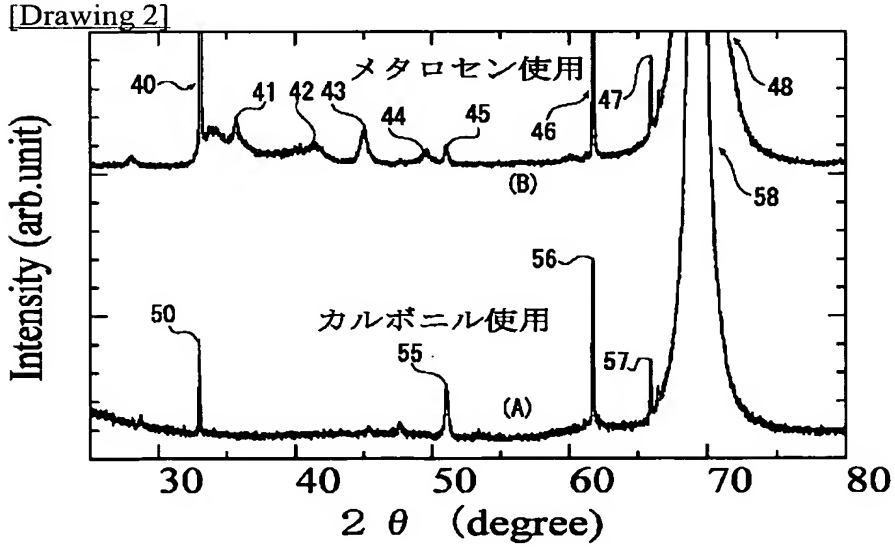
DRAWINGS

[Drawing 1]



[Drawing 2]



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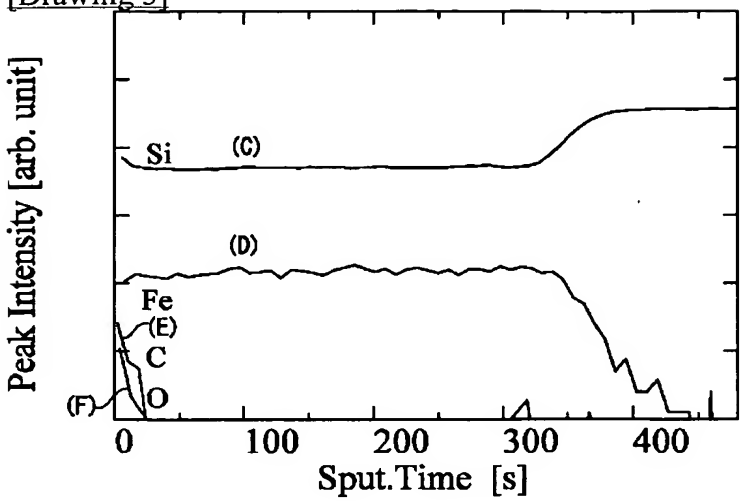
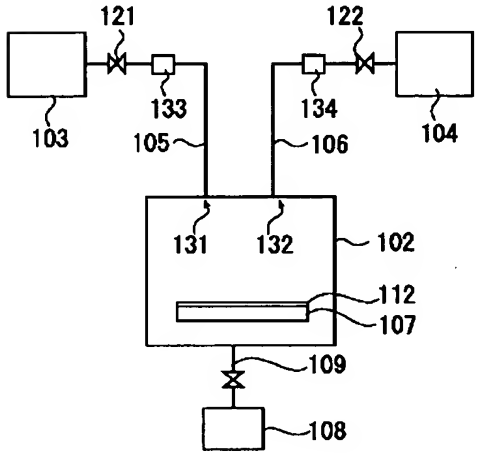


[Drawing 6]



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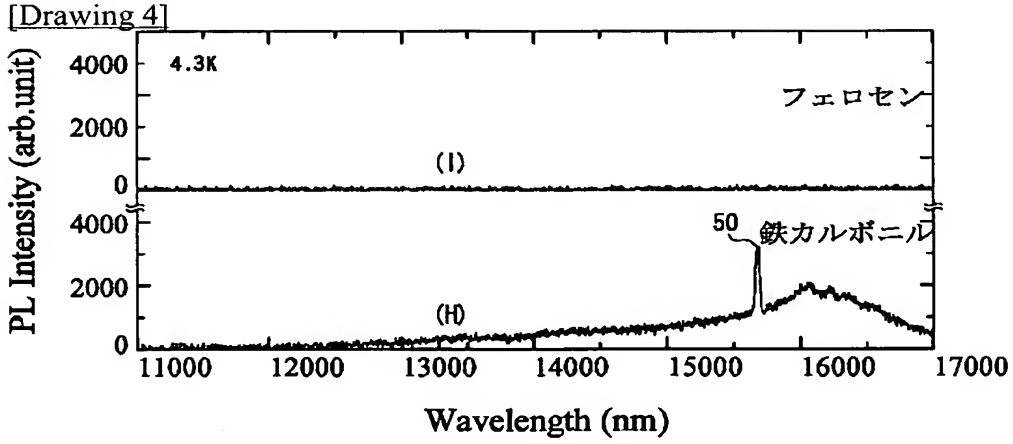
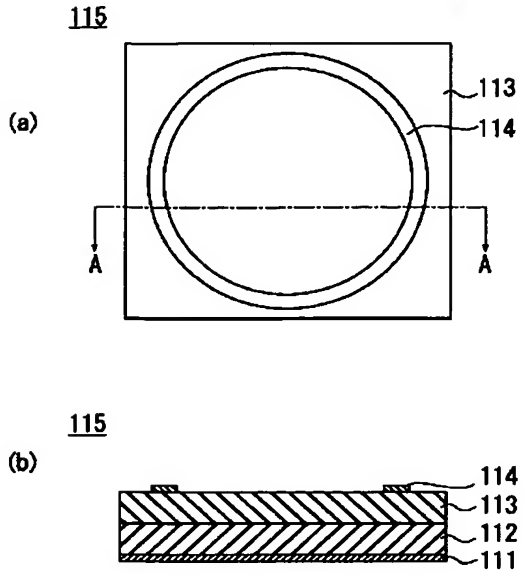


[Drawing 5]



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